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Permanent Carbon Dioxide Storage into Basalt: The CarbFix Pilot Project, Iceland

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Abstract

The storage of large volumes of industrial CO_2 emissions in deep geological formations is one of the most promising climate mitigation options. The long-term retention time and environmental safety of the CO_2 storage are defined by the interaction of the injected CO_2 with the reservoir fluids and rocks. Finding a storage solution that is long lasting, thermodynamically stable and environmentally benign would be ideal. Storage of CO_2 as solid magnesium or calcium carbonates in basaltic rocks may provide such a long-term and thermodynamically stable solution. Basaltic rocks, which primarily consist of magnesium and calcium silicate minerals, provide alkaline earth metals necessary to form solid carbonates. In nature, the carbonization of basaltic rocks occurs in several well-documented settings, such as in the deep ocean crust, through hydrothermal alteration and through surface weathering. The goal of the CarbFix pilot project is to optimize industrial methods for permanent storage of CO_2 in basaltic rocks. The objective is to study the in-situ mineralization of CO_2 and its long term fate. The project involves the capture and separation of flue gases at the Hellisheidi Geothermal Power Plant, the transportation and injection of the CO_2 gas fully dissolved in water at elevated pressures at a depth between 400 and 800 m, as well as the monitoring and verification of the storage. A comprehensive reservoir characterization study is on-going prior to the CO_2 injection, including soil CO_2 flux measurements, geophysical survey and tracer injection tests. Results from the tracer tests show significant tracer dispersion within the target formation, suggesting large surface area for chemical reactions. The large available reservoir volume and surface area in combination with relatively rapid CO_2-water-rock reactions in basaltic rocks may allow safe and permanent geologic storage of CO_2 on a large scale.

Keywords: Geologic CO_2 storage; in-situ mineral carbonation; geochemical monitoring and verification

1. Introduction

Minimizing climate change impacts from increasing atmospheric CO_2 concentrations calls for dramatic reductions in anthropogenic CO_2 emissions if stabilization is to be accomplished [1-3]. Carbon capture and storage has been proposed as one means to reduce CO_2 emissions from utilizing fossil fuels [4]. The technology involves the capture of CO_2 emissions and the storage in suitable reservoirs. Storage in geologic reservoirs, such as depleted oil and gas reservoirs and deep saline aquifers in sedimentary basins at depths typically >800 m, has been studied extensively over the last decade [4, 5-9]. An alternative storage option is the conversion of CO_2 gas into stable carbonate minerals such as calcite ($CaCO_3$), dolomite ($CaMgCO_3$), magnesite ($MgCO_3$) and siderite ($FeCO_3$). Mineral carbonation can be carried out *ex-situ* in a processing plant or *in-situ* in silicate-rich geological formations [4, 10]. Basalt or peridotite have been considered as promising reactants for *in-situ* mineralization of CO_2 because of high concentrations of calcium, magnesium silicate minerals in these type of rocks [10-14]. McGrail et al. [11] showed that kilometer-scale interflow zones in the Columbia River Basalt Group lava flows have significant porosity and lateral connectivity for large volume CO_2 injection. In addition, low-permeability interbedded sediments and the impermeable massive basalt between the interflow zones provide a barrier for vertical CO_2 migration. Goldberg et al. [12] demonstrated large storage capacity of sub-oceanic basalt formations. Contrary to the general assumption that fluid-rock reactions are slow, calculations as well as laboratory and small scale field experiments showed relatively rapid CO_2 neutralization and mineralization rates in

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basaltic rocks [10,11,13,15,16]. However, *in-situ* mineral carbonation is not without challenges. CO_2 dissolution into groundwater is slow and limits the mineral dissolution and precipitation reactions. Slow reactions require an impermeable cap rock above the injection reservoir to keep the dissolved CO_2 in contact with the reactive rocks and to prevent leakage. Furthermore, mobilization of toxic metals as a result of CO_2-water-rock interaction may lead to their migration within the reservoir. The chemical reactivity of these metals within the reservoir has to be addressed.

Up to date, the potential of CO_2 storage in basaltic rocks have been demonstrated on a limited scale. In an attempt to gain further insight into *in-situ* mineral carbonation in basaltic rocks on a larger scale, the CarbFix pilot project was launched in 2007 [17]. In this paper we discuss in-situ mineral carbonation in basaltic rocks and provide a technical and scientific overview of the CarbFix project.

2. *In-situ* mineral carbonation

Mineral carbonation requires divalent metallic cations, such as Ca^{2+}, Mg^{2+} and Fe^{2+} for the carbonation process. When CO_2 reacts with Ca, Mg, Fe oxides, the corresponding carbonate is formed and heat is released. These oxides are prevalent in silicate minerals. Given the concentration of the oxides and their reactivity, focus on in-situ mineral carbonation has been on rocks rich in olivine, serpentine, pyroxene, plagioclase feldspar and basaltic glass. Crystalline basalt is rich in plagioclase feldspars, pyroxene and olivine, and basalt, glassy and crystalline, contains 7-10 wt% Ca, 5-6 wt% Mg, and 7-13 wt% Fe. After injection of CO_2 in deep aquifers in basaltic rocks following exothermic chemical reactions are taking place:

$$(Ca^{2+}, Mg^{2+}) + CO_2 + H_2O = (Ca, Mg)CO_3 + 2H^+ \quad (1)$$

Groundwater in basaltic rock is rich in divalent metallic cations, which may react with CO_2 to precipitate carbonate minerals according to reaction (1). Per mol of carbonate minerals precipitated, 2 moles of H^+ ions are produced. This reaction will not proceed to the right unless the H^+ ions are neutralized. Neutralization of H^+ will take place by reaction with the primary mineral phases in the basaltic host rock, as simplified in reaction (2) and (3).

$$Mg_2SiO_4 + 4H^+ \rightarrow 2Mg^{2+} + 2H_2O + SiO_2 \quad (2)$$

Forsterite

$$CaAl_2SiO_8 + 2H^+ + H_2O \rightarrow Ca^{2+} + Al_2Si_2O_5(OH)_4 \quad (3)$$

Ca-plagioclase

The precipitation of carbonate minerals is pH dependent as the acidity of the solution (i.e. H^+ concentration) controls the carbonate ion concentration in solution. The dissolution of basalt minerals and the release of divalent metallic cations cause the pH of the solution to rise until carbonate precipitation begins. Since the precipitation kinetics of calcite is known to be fast (1), the extent of mineral carbonation is determined by the dissolution kinetics of reaction (2) and (3).

There is evidence for the potential of mineral carbonation in basaltic rocks. There are enormous volumes of basaltic rocks present on Earth's surface with a correspondingly large CO_2 storage capacity. The Columbia River Basalt with a total volume >200,000 km^3 has an estimated storage capacity in excess of 100 Gt of CO_2 [11], whereas deep-sea basalt aquifers such as the one on the Juan de Fuca plate could potentially store over 700 Gt of CO_2 [12]. The chemical reactivity and the carbonation potential of basalt is demonstrated by surface weathering processes [16-20], as well as by the fast release rate of Ca and Mg ions when reacted with CO_2-rich waters [13]. The flux of Ca and Mg from basaltic rocks is up to two orders of magnitude larger than from other silicate-rich rocks [21]. Concerning the carbonation of basalt, studies of natural analogues on water-basalt-reactions at low P_{CO2} conditions showed calcite, clays, zeolites and quartz/chalcedony as the dominant secondary minerals [22], whereas quartz and Fe, Mg-, and Ca-carbonates are dominate under high P_{CO2} conditions [23].

3. The CarbFix Project, Iceland

The CarbFix project is a multinational research project with the primary goal to imitate the natural storage process of CO_2 observed in basaltic rocks on a field scale (http://www.carbfix.com). The project was established by Icelandic, French and American scientists and was officially launched in 2007. The main partners in the project are Reykjavik Energy, as the main sponsor, University of Iceland, The Earth Institute at Columbia University in New York, and Centre National de la Recherche Scientifique Univesité Paul Sabatier in France. The project consists of a field-scale CO_2 injection into basalt, laboratory experiments on dissolution and precipitation kinetics, geochemical modeling, and study of natural CO_2-rich waters as a natural analogue.

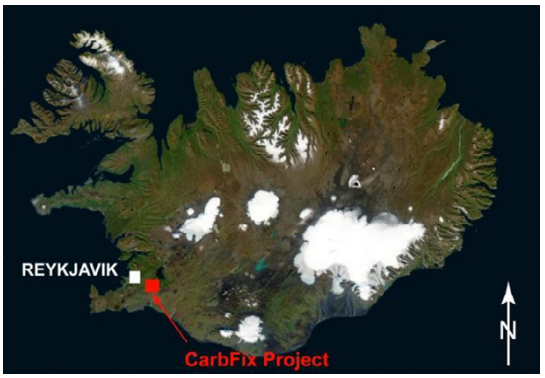

Figure 1: Satelitte image of Iceland indicating the location of the CarbFix Site.

The field site is situated in SW Iceland, close to the Hellisheidi geothermal power plant (Figure 1). The geothermal power plant produces up to 30,000 tons of CO_2 per year, although this number will increase as the plant expands. The source of the CO_2 is the geothermal gas which is a by product of the geothermal steam production. The geothermal steam contains around 1% of geothermal gases, which is composed of CO_2 (83%), H_2S (16%) and CH_4, N_2, and H_2 (together 1%). The different geothermal gases will be separated in a pilot gas processing plant, which is under construction. The gases coming from the condenser will be compressed and cooled. The CO_2 and H_2S will be separated and the H_2S will be re-injected with the geothermal water into the deep geothermal reservoir. The CO_2 with 2% of H_2S will be available for the injection into the basalt aquifer. In addition, the H_2 component in the geothermal gas will be separated from the gas mixture by membranes and will be available for the market.

The CO_2 injection site comprises of one injection well with a total depth of 2000 m and several vertical and inclined observation wells with total depths between 100 and 1400 m (Figure 2).

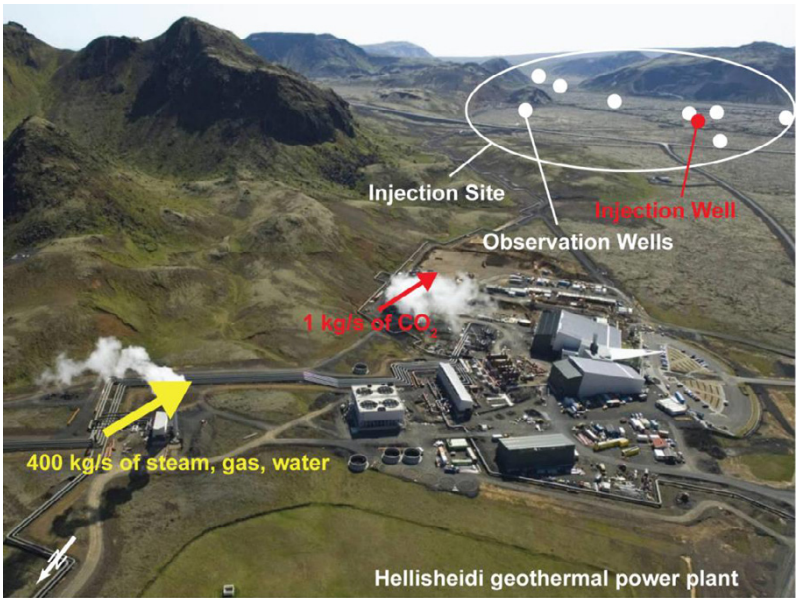

Figure 2: Air photograph from the injection site. The geothermal power plant as the source of the CO_2 is approximately 3 km to the north of the injection site. The injection site includes one injection well and several observation wells.

The target injection formation at a depth of 400 to 800 m consists of basaltic lava flows and hyaloclastite [24]. Figure 3 shows a N-S cross section of the injection site, including the existing borehole infrastructure. The temperature at injection depth interval is between 30ºC and 50ºC. Some of the observation wells cut into the target injection reservoir, whereas others are shallow wells in the shallow aquifer (Figure 3). Additional observation wells are situated to the North of the injection site. This setup of observation wells will allow the monitoring of the injection reservoir as well as the shallow aquifer along the hydraulic gradient. CO_2 will be injected at a partial pressure of around 25 bars and at a rate of 0.5 to 0.7 kg/s for a time period of 6 months. Since mineral carbonation requires dissolution of CO_2 into an aqueous solution, groundwater will be injected simultaneously with CO_2 at a rate of approximately 20-25 l/s. This will require a large volume of water. Dissolution of one ton of CO_2 at 25 bars partial pressure and 25ºC requires approximately 27 tons of water [10]. An alternative would be to inject dry CO_2. In such an injection scenario, mineral carbonation is expected to be slower since the CO_2 has to dissolve into the groundwater to be chemically reactive. Because water availability is not an issue in Iceland, CO_2 and water are simultaneously injected in the CarbFix project with the goal to speed up *in-situ* CO_2 mineralization.

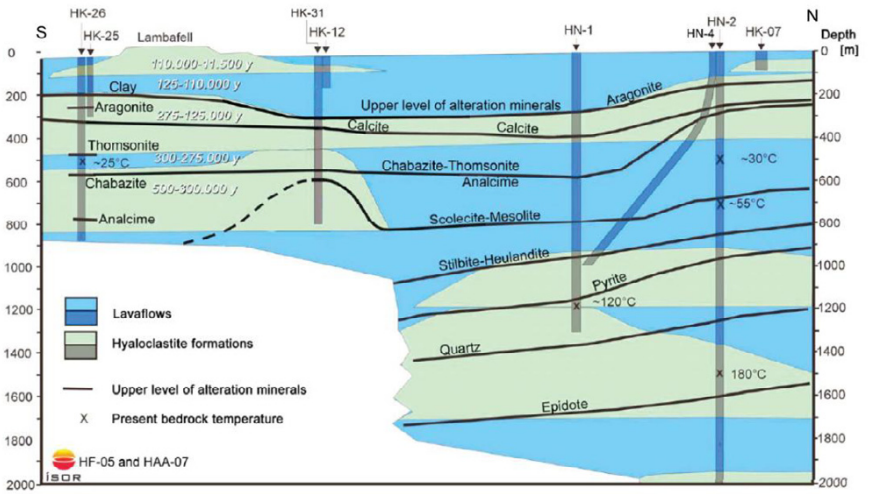

Figure 3: N-S geological cross section of the injection site, including injection well (HN-2) and monitoring wells. The injection interval at a depth between 400-800 m consists of lava flows and hyaloclastite (basaltic glass) formations (Alfredsson et al. [24]).

Prior to the CO_2 injection, which will begin early in 2009, a pre-CO_2 injection field characterization study is ongoing. The goal is to understand the hydrogeology and geology of the target reservoir and the overlying formations. Various methods have been applied since 2007; including soil CO_2 flux measurements, systematic monitoring of groundwater chemistry and borehole geophysical measurements (resistivity, natural gamma, flowmeter, acoustic televiewer). In addition, two tracer tests have been conducted within the injection reservoir. A preliminary tracer test, using Na-fluorescent dye as a conservative tracer, was carried out from November 2007. In addition, a large scale tracer test with sulfur hexafluoride (SF_6) and Na-fluorescent dye is ongoing since June 2008. The preliminary tracer test was conducted as a forced gradient test between two nearby wells, HN-2 and HN-4. A flow field between the two wells was induced by continuous injection of water at a rate of 5 kg/s in well HN-2 and pumping of water at a rate of 10 kg/s from well HN-4 (Figure 3). The distance between the two wells is 60 m at 400 m depth and 360 m at 600 m depth (note that well HN-4 is inclined). According to Khalilabad et al. [25], the analysis and interpretation of the preliminary tracer test revealed that preferential flow paths within the target reservoir exist but that most of the basaltic bedrock consists of relatively homogeneous porous media (Figure 4). Thus, a uniform network of interconnected pore space may provide high tortuosity and large reactive surface area for CO_2-water-rock interaction.

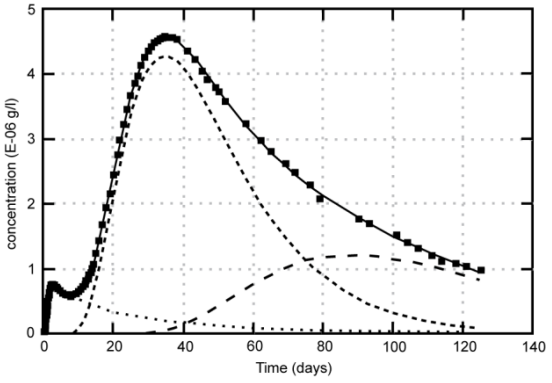

Figure 4: Observed and simulated Na-fluorescein recovery in one observation well. The simulated recovery curves assume three distinct flow paths (modified from Khalilabad et al. [25])

For the large scale tracer test, 50 kg of Na-fluorescent dye and ~14 g or SF_6, each dissolved in 1 m^3 of groundwater, were injected as a slug into the injection reservoir to study solute transport under natural groundwater flow conditions. Unlike in the preliminary tracer test, no flow field was induced by pumping. The results of this test will allow the quantification of transport parameters and measurement of subsurface properties, which are important input parameters for the numerical simulations of the CO_2 injection. In addition, potential detection of these tracers in the shallow aquifer will provide information about the hydraulic connection between the injection reservoir and overlying formations.

4. Summary and Perspectives

Understanding the long-term fate of CO_2 injected into geological reservoirs for the purpose of carbon storage is crucial for the success of this carbon mitigation option. Injection of large volumes of CO_2 will greatly perturb the subsurface environment leading to changes in physical, geochemical and biogeochemical parameters. These changes will be the driving force for unknown processes that may enhance or impede permanent storage of CO_2. In-situ mineral carbonation in basaltic rocks offers the potential for permanent and safe storage of CO_2. It, however, requires a better geological and hydrogeological characterization of basalt formations in terms of fluid flow and solute transport, a more accurate quantification of reaction kinetics of mineral and

glass dissolution and mineral carbonation reactions at relevant P/T conditions, as well as the development and testing of monitoring techniques suitable for reactive rock systems. The verification that the injected CO_2 has been fixed in carbonate minerals on a relevant time scale, and that leakage is a minimal risk will be of great importance for the success of in-situ mineral carbonation as an alternative storage option. The CarbFix project addresses these challenges with a multifaceted approach, including a field-scale pilot injection of CO_2 charged waters into a permeable basalt formation, laboratory based experiments, the study of natural CO_2-rich waters as a natural analogue, and reactive transport modeling studies.

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References

[1] Hoffert, M. I., et al. (2002), Advanced technology paths to global climate stability: Energy for a greenhouse planet. Science 298, 981–987.
[2] Pacala, S., and R. Socolow (2004), Stabilization wedges: Solving the climate problem for the next 50 years with current technologies. Science 305, 968–971.
[3] IPCC (2007), Summary for Policymakers. In: *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M.Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
[4] Metz B., O. Davidson, H. de Coninck, M. Loos, and L. Meyer (eds), *IPCC Special Report on Carbon Dioxide Capture and Storage,* Cambridge University Press, New York, 2005.
[5] Bachu S., W. D. Gunter, and E. H. Perkins (1994), Aquifer disposal of CO_2: Hydrodynamic and mineral trapping. Energy Convers. Manag., 35(4), 269–279.
[6] Gunter W. D., B. Wiwchar, and E. H. Perkins (1997), Aquifer disposal of CO2–rich greenhouse gases: Extension of the time scale of experiment for CO_2–sequestering reactions by geochemical modeling, Mineral. Petrol., 59(1–2), 121–140.
[7] Korbol R., and A. Kaddour (1999), Sleipner West CO_2 disposal–injection of removed CO_2 into the Utsira formation. Energy Convers Manage 36(3–9), 509–12.
[8] Jessen K., A.R. Kovscek, and F.M. Orr Jr. (2005), Increasing CO_2 storage in oil recovery. Energy Convers Manage 46(2), 293–311.
[9] Hovorka S.D, S.M. Benson, C. Doughty, B.M. Freifeld, S. Sakurai, T.M. Daley, Y.K. Kharaka, M.H. Holtz, R.C. Trautz, H.S. Nance, L.R. Myer, and K.G. Knauss (2006), Measuring permanence of CO_2 storage in saline formations: the Frio experiment. Environmental Geosciences 13, 105-121.
[10] Oelkers E.H., S.R. Gislason, and J. Matter (2008), Mineral Carbonation of CO_2, Elements, Vol. 4, 331-335.
[11] McGrail B.P., H.T. Schaef, A.M. Ho, Y.J. Chien, J.J. Dooley, and C.L. Davidson (2006), Potential for carbon dioxide sequestration in flood basalts. Journal of Geophysical Research 111: B12201.
[12] Goldberg D.S., T. Takahashi, and A.L. Slagle (2008), Carbon dioxide sequestration in deep-sea basalt. Proceedings of the National Academy of Sciences 105, 9920-9925.
[13] Matter J.M., T. Takahashi, and D. Goldberg (2007), Experimental evaluation of in situ CO_2-water-rock reactions during CO_2 injection in basaltic rocks. Implications for geological CO_2 sequestration. Geochemistry, Geophysics, Geosystems 8: doi 10.1029/2006GC001427.
[14] Kelemen P., and J.M. Matter (2008), In situ carbonation of peridotite for CO_2 storage. Proceedings of the National Academy of Sciences (in press).
[15] Marini L. (2007), Geological Sequestration of Carbon Dioxide: Thermodynamics, Kinetics, and Reaction Path Modeling. Elsevier, Amsterdam, 470 pp.
[16] Gysi A.P., and A. Stefánsson (2008). Numerical modeling of CO_2-water-basalt interaction. Mineralogical Magazine, Vol. 71(1), 55-59.
[17] Sigurðardóttir H. (2008), Nature imitated in permanent CO_2 storage project in basalts in Iceland. Greenhouse Issues, June 2008, 15-17.
[18] Gislason S., and H.P. Eugster (1987), Meteoric water-basalt interactions: II. A field study in NE Iceland. Geochimica et Cosmochimica Acta 51, 2841-2855.
[19] Gislason S.R., S. Arnórsson, and H. Ármannsson (1996), Chemical weathering of basalt in Southwest Iceland: Effects of runoff, age of rocks and vegetative/glacial cover. American Journal of Science 296, 837-907.
[20] Léveillé R.J., W.S. Fyfe, and F.J. Longstaffe (2000), Unusual secondary Ca-Mg-carbonate-kerolite deposits in basaltic caves, Kauai, Hawaii. The Journal of Geology, Vol. 108, 613-621.

[21] Wolff-Boenisch D., S.R. Gislason, and E.H. Oelkers (2006), The effect of crystallinity on dissolution rates and CO_2 consumption capacity of silicates. Geochimica et Cosmochimica Acta 70, 858-870.
[22] Neuhoff P.S., T. Fridriksson, S. Arnorsson, and D.K. Bird (1999), Porosity evolution and mineral paragenesis during low-grade metamorphism of basaltic lavas at Teigarhorn, eastern Iceland. American Journal of Science 299, 467-501.
[23] Roger K.L., P.S. Neuhoff, A.K. Pedersen, and D.K. Bird (2006), CO_2 metasomatism in a basalt-hosted petroleum reservoir, Nuussuaq, West Greenland. Lithos, 92, 55-82.
[24] Alfredsson H.A., B.S. Hardarson, H. Franzson, and S.R. Gislason (2008), CO_2 sequestration in basaltic rock at the Hellisheidi site in SW Iceland: stratigraphy and chemical composition of the rocks at the injection site. Mineralogical Magazine, Vol. 72(1), 1-5.
[25] Khalilabad M.R, G. Axelsson, and S.R. Gislason (2008), Aquifer characterization with tracer test technique; permanent CO_2 sequestration into basalt, SW Iceland. Mineralogical Magazine, Vol. 71(1), 121-125.